# DYES

The extraction and preparation of dyestuffs, mentioned in Chinese literature as long ago as 3000 B.C., may have been man's earliest attempts at the practice of chemistry. Early dyes were obtained mainly from plants: their roots, leaves, bark, or berries.

Blue, in particular, was a much-sought-after color. Compared with red and yellow, blue shades are not common in plants, but one plant, Indigofera tinctoria, a member of the legume family, was known to be a major source of the blue dye indigo.

Fig 1. The indigo plant

On his travels seven hundred years ago, Marco Polo was reputed to have seen indigo being used in the Indus valley; hence the name indigo. But indigo was also prevalent in many other parts of the world, including Southeast Asia and Africa, well before the time of Marco Polo.

The fresh leaves of indigo-producing plants do not appear to be blue. But after fermentation under alkaline conditions followed by oxidation, the blue color appears.

The indigo precursor compound, found in all indigo-producing plants, is indican, a molecule that contains an attached glucose unit. Indican itself is colorless, but fermentation under alkaline conditions splits off the glucose unit to produce the indoxol molecule. Indoxol reacts with oxygen from the air to produce blue-colored indigo (or indigotin, as chemists call this molecule).

Fig 2. Indigo colored fabric

Indigo was a very valuable substance, but the most expensive of the ancient dyes was a very similar molecule known as Tyrian purple. In some cultures the wearing of purple was restricted by law to the king or emperor; hence the other name for this dye—royal purple—and the phrase "born to the purple," implying an aristocratic pedigree. Even today purple is still regarded as an imperial color, an emblem of royalty.

Tyrian purple colored the robes of Roman senators, Egyptian pharaohs, and European nobility and royalty. It was so sought after that by A.D. 400 the species of shellfish that produced it were in danger of becoming extinct.

Indigo and Tyrian purple were manufactured by these labor-intensive methods for centuries. It was not until the end of the nineteenth century that a synthetic form of indigo became available. In 1865 the German chemist Johann Friedrich Wilhelm Adolf von Baeyer began investigating the structure of indigo.

By 1880 he had found a way to make it in the laboratory from easily obtainable starting materials. It took another seventeen years, however, before synthetic indigo, prepared by a different route and marketed by the German chemical company Badische Anilin und Soda Fabrik (BASF), became commercially viable.

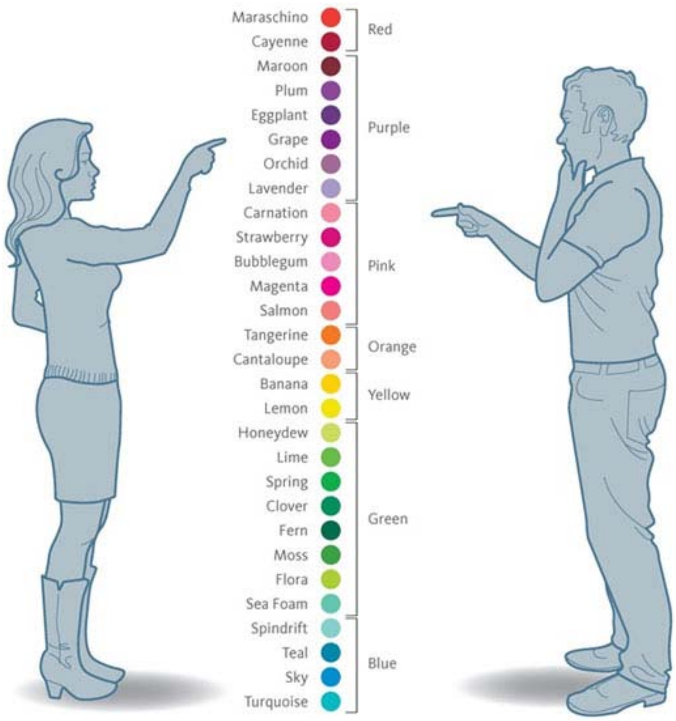


Fig 3. Different colors

Today an annual production of over fourteen thousand tons makes synthetic indigo a major industrial dye. Though synthetic indigo (like the natural compound) notoriously lacks colorfastness, it is most often used to dye blue jeans, where this property is considered a fashion advantage.

Dyes are colored organic compounds that are incorporated into the fibers of textiles. The molecular structure of these compounds allows the absorption of certain wavelengths of light from the visible spectrum. The actual color of the dye we see depends on the wavelengths of the visible light that is reflected back rather than absorbed. If all the wavelengths are absorbed, no light is reflected, and the color of the dyed cloth we see is black; if no wavelengths are absorbed, all light is reflected and the color we see is white. Dyes have long been associated with army uniforms. The blue coats supplied by France to the Americans during the American Revolution were dyed with indigo.

Cochineal was a dye of the New World, used by the Aztecs long before the arrival of the Spanish conquistador Hernán Cortés in 1519. Cortés introduced cochineal to Europe, but its source was kept secret until the eighteenth century, in order to protect the Spanish monopoly over this precious scarlet dye. Later, British soldiers became known as “redcoats” from their cochineal-dyed jackets. Cochineal, also called carmine, was expensive. It took about seventy thousand insect bodies to produce just one pound of the dye. Today the major producer of the dye is Peru, which makes about four hundred tons annually, around 85 percent of the world’s production. The Aztecs were not the only people to use insect extractions as dyes. Ancient Egyptians colored their clothes (and the women their lips) with red juice squeezed from the bodies of the kermes insect (Coccus ilicis). The red pigment from this beetle is mainly kermesic acid, a molecule extraordinarily similar to its New World counterpart of carminic acid from cochineal. But unlike carminic acid, kermesic acid never went into widespread use.


Fig 4. “Redcoats”

Although kermesic acid, cochineal, and Tyrian purple were derived from animals, plants supplied most of the starting materials for dyers.

Once widespread over Europe, saffron growing declined during the Industrial Revolution for two reasons. First, the three stigmas in each hand-picked blossom had to be individually removed. This was a very labor-intensive process, and laborers at this time had largely moved to the cities to work in factories. The second reason was chemical. Although saffron produced a beautiful brilliant shade, especially when applied to wool, the color was not particularly fast. When man-made dyes were developed, the once-large saffron industry faded away. Saffron is still grown in Spain, where each flower is still hand-picked in the traditional way and at the traditional time, just after sunrise. The majority of the crop is now used for the flavoring and coloring of food in such traditional dishes as Spanish paella and French bouillabaise. Because of the way it is harvested, saffron is the most expensive spice in the world today; thirteen thousand stigmas are required to produce just one ounce.

By 1856 eighteen-year-old William Henry Perkin had synthesized an artificial dye that radically changed the dye industry. Perkin was a student at London's Royal College of Chemistry; his father was a builder who had little time for the pursuit of chemistry because he felt it was unlikely to lead to a sound financial future. But Perkin proved his father wrong. Over his Easter holidays of 1856, Perkin decided to try to synthesize the antimalarial drug quinine, using a tiny laboratory that he had set up in his home. His teacher, one August Hofmann, a German chemistry professor at the Royal College, was convinced that quinine could be synthesized from materials found in coal tar, the same oily residue that was, a few years later, to yield phenol for surgeon Joseph Lister. The structure of quinine was not known, but its antimalarial properties were making it in short supply and great demand. The British Empire and other European nations were expanding their colonies into malaria-ridden areas of tropical India, Africa, and Southeast Asia. The only known cure and preventive for malaria was quinine, obtained from the increasingly scarce bark of the South American cinchona tree. A chemical synthesis of quinine would be a great achievement, but none of Perkin's experiments were successful. One of his trials did, however, produce a black substance that dissolved in ethanol to give a deep purple solution. When Perkin dropped a few strips of silk into his mixture, the fabric soaked up the color. He tested this dyed silk with hot water and with soap and found that it was colorfast. Perkin exposed the samples to light; the color did not fade—it remained a brilliant lavender purple. Aware that purple was a rare and costly shade in the dye industry and that a purple dye, colorfast on both cotton and silk, could be a

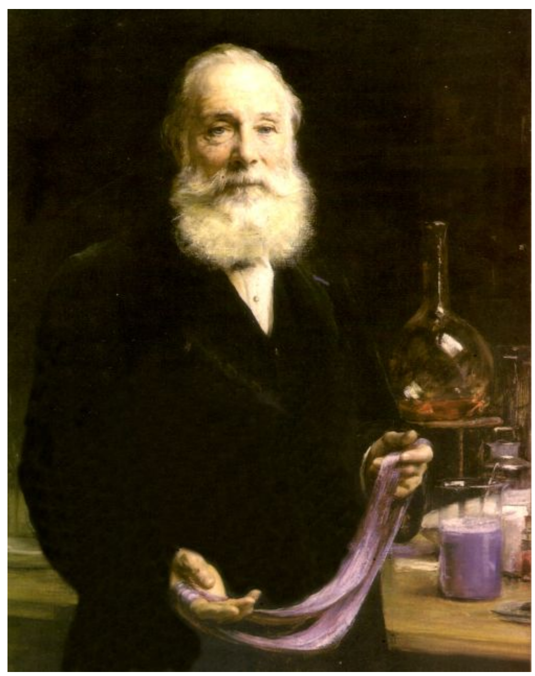

Fig 5. William Henry Perkin

commercially viable product, Perkin sent a sample of the dyed cloth to a leading dyeing company in Scotland. Back came a supportive reply: “If your discovery does not make the goods too expensive, it is decidedly one of the most valuable that has come out for a very long time.”

This was all the encouragement Perkin needed. He left the Royal College of Chemistry and, with financial help from his father, patented his discovery, set up a small factory to produce his dye in larger quantities and at a reasonable cost, and investigated the problems associated with dyeing wool and cotton as well as silk. By 1859 mauve, as Perkin’s purple was called, had taken the fashion world by storm. Mauve became the favorite color of Eugénie, empress of France, and the French court.

The dye trade, which now mainly produces chemically synthesized artificial dyes, became the forerunner to an organic chemical enterprise that would eventually produce antibiotics, explosives, perfumes, paints, inks, pesticides, and plastics.